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# Pulsed laser deposition (PLD) of a CZTS-absorber for thin solar cells with up to 5.2 % efficiency

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## Introduction:

Pulsed laser deposition (PLD) is usually considered as a technique, by which a complicated material can be transferred from a target to a substrate with the same stoichiometry. It is widely used in scientific labs, in particular for production of complex oxide films. PLD is a non-equilibrium film deposition technique, and since the energy source is outside the deposition chamber, the parameter space is huge for all physical parameters such as the background gas pressure, the substrate temperature, the target-substrate distance and the laser fluence. We are investigating PLD of thin films of chalcogenide materials  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) and  $\text{Cu}_2\text{SnS}_3$  (CTS), which are promising candidates for absorber layers of earth-abundant thin-film solar cells. The material transfer is found highly non-stoichiometric, contrary to what is commonly believed with PLD.

We investigate deviations from stoichiometry and find out that:

- 1) Copper content increases with increasing fluence.
- 2) Droplets density and size increase with laser fluence.

Lambda	Energy - p.r.r.	Pressure	T <sub>subs</sub>
248 nm	30mJ - 10 Hz	<10 <sup>-7</sup> mbar	RT to 300 C

Results shown here are published in:  
A.Cazzaniga et al.  
Solar Energy Materials and Solar Cells:  
**166**, 91-99 (2017)

**Experimental:** We deposit a thin layer of CZTS (or CTS) onto Mo-coated Soda Lime Glass by Pulsed laser Deposition (PLD) in high vacuum. The targets are made of sintered powders and are not single phase. They contain mostly binary phases CuS, ZnS and SnS, which have different thermal properties and vapor pressure. The CZTS films were deposited with PLD at room temperature at DTU and treated with standard annealing at 560 C at UNSW.

**Why using PLD?** PLD allows single step deposition of materials of complex stoichiometry from the highly nonthermal removal of target material. Crystallinity of the film can be enhanced even at modest substrate temperatures as compared to other techniques such as evaporation deposition due to the non-thermal energy of the arriving atoms.

CZTS film on substrate

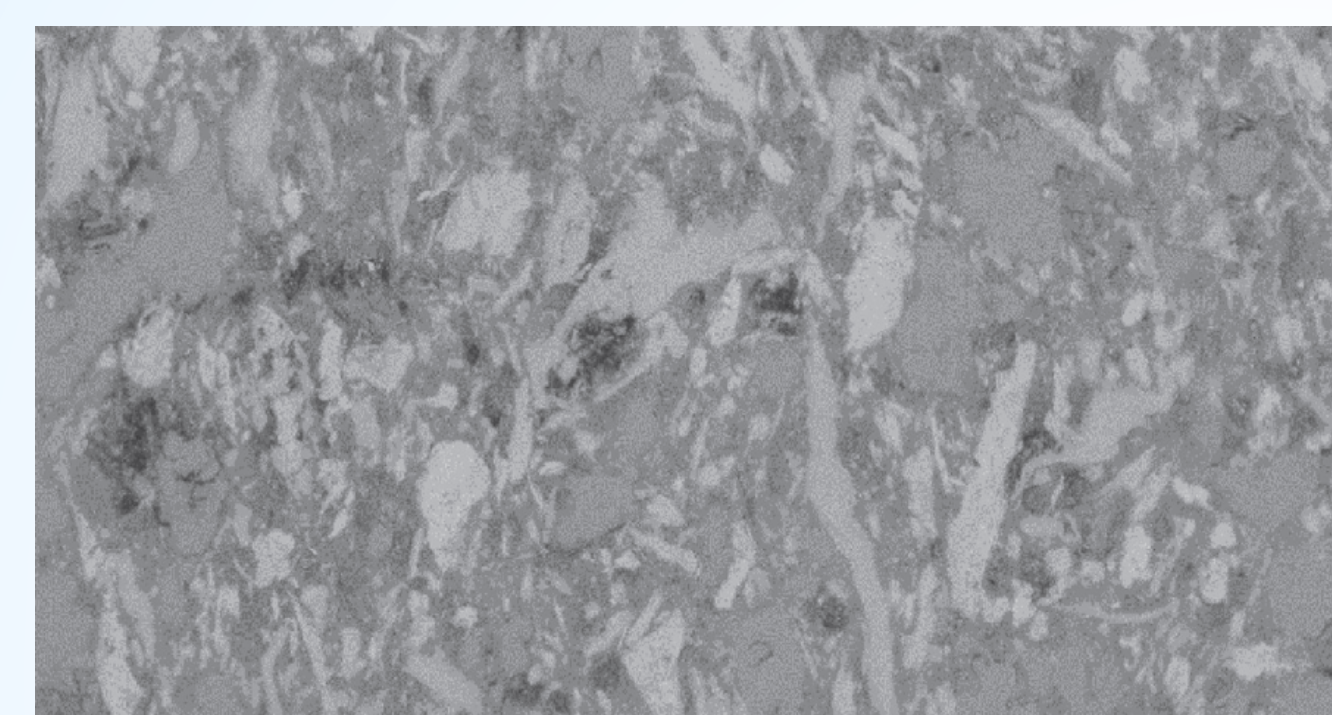
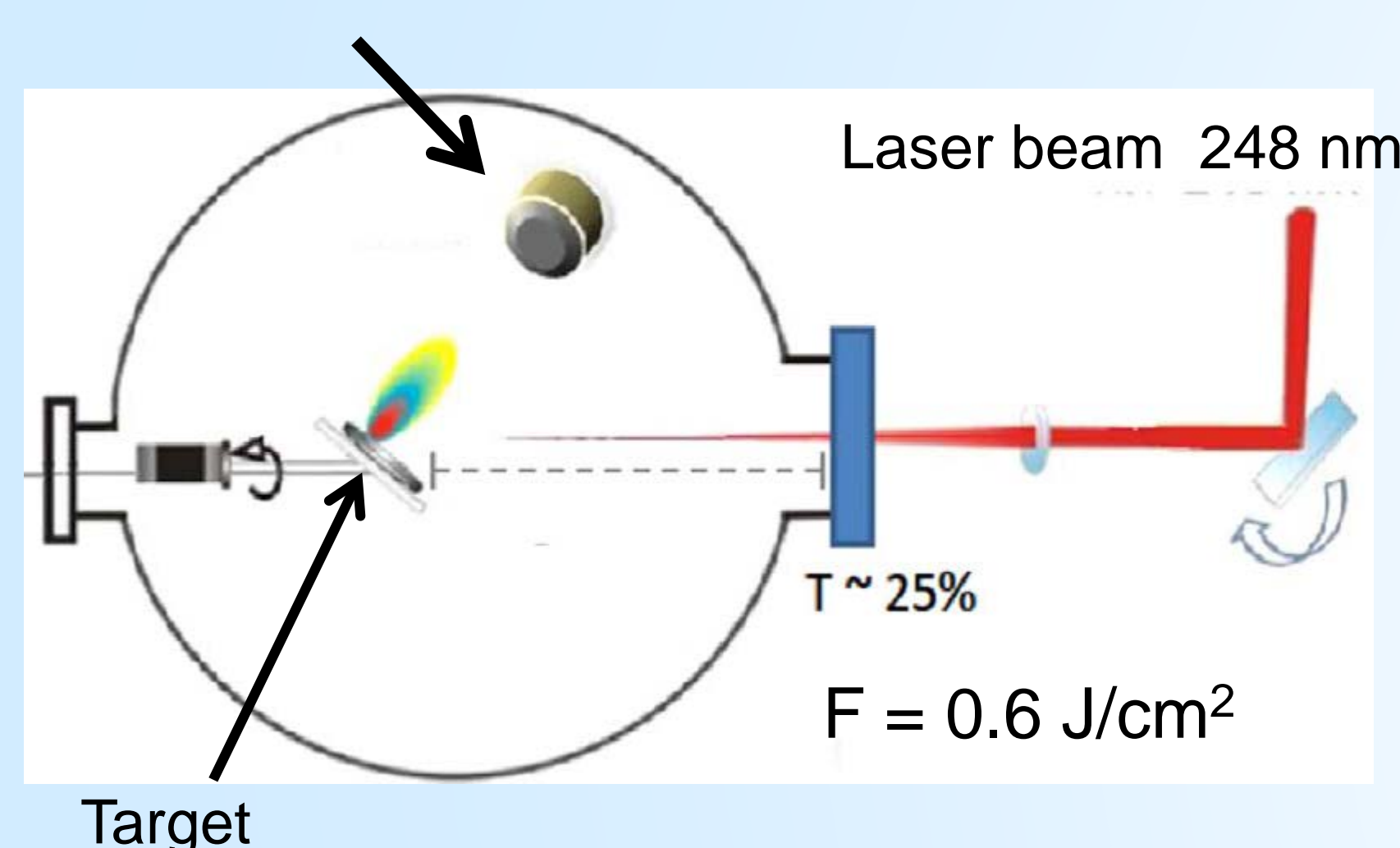
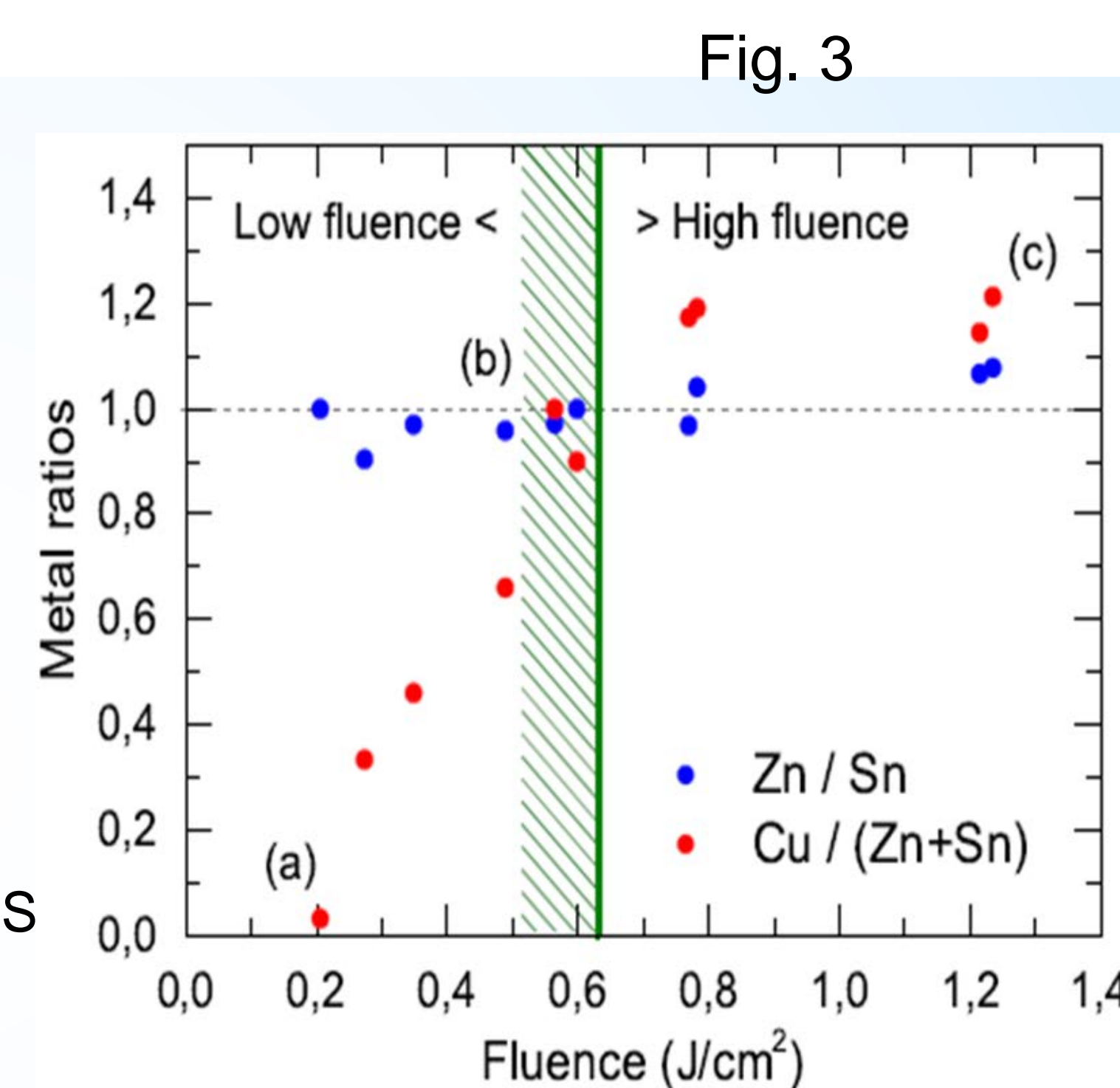


Fig. 2 SEM image of the CZTS (2CuS:ZnS) sintered target.

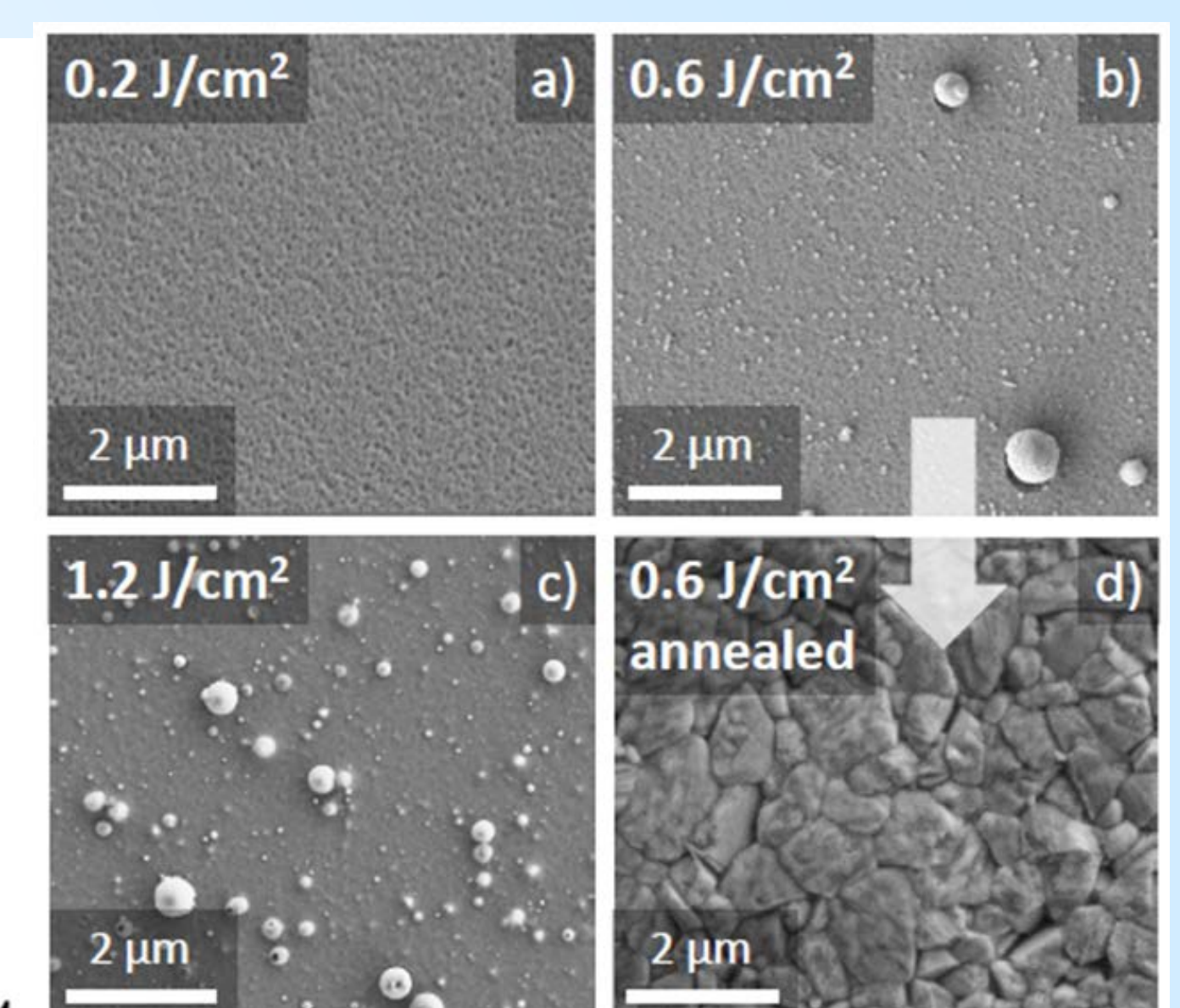
**Fig. 1** The fluence on the target was 0.6 J/cm² with a spot size of 4 mm².

**Fig. 2** The different phases over a typical length scale of a few hundred μm are clearly visible



**Fig. 3:** Non-stoichiometric material transfer as function of laser fluence. Copper content varies significantly, while Zn and Sn are kept in stoichiometric proportion (within EDX detection limit, grey bar). S content not shown for clarity.

Fig.



**Fig. 4** Droplets on films at different fluence. No peaks detected in XRD, indicating the films and the droplets are amorphous

**Fig. 5:** The champion CZTS film deposited with PLD at RT and subsequently annealed at 560 C.

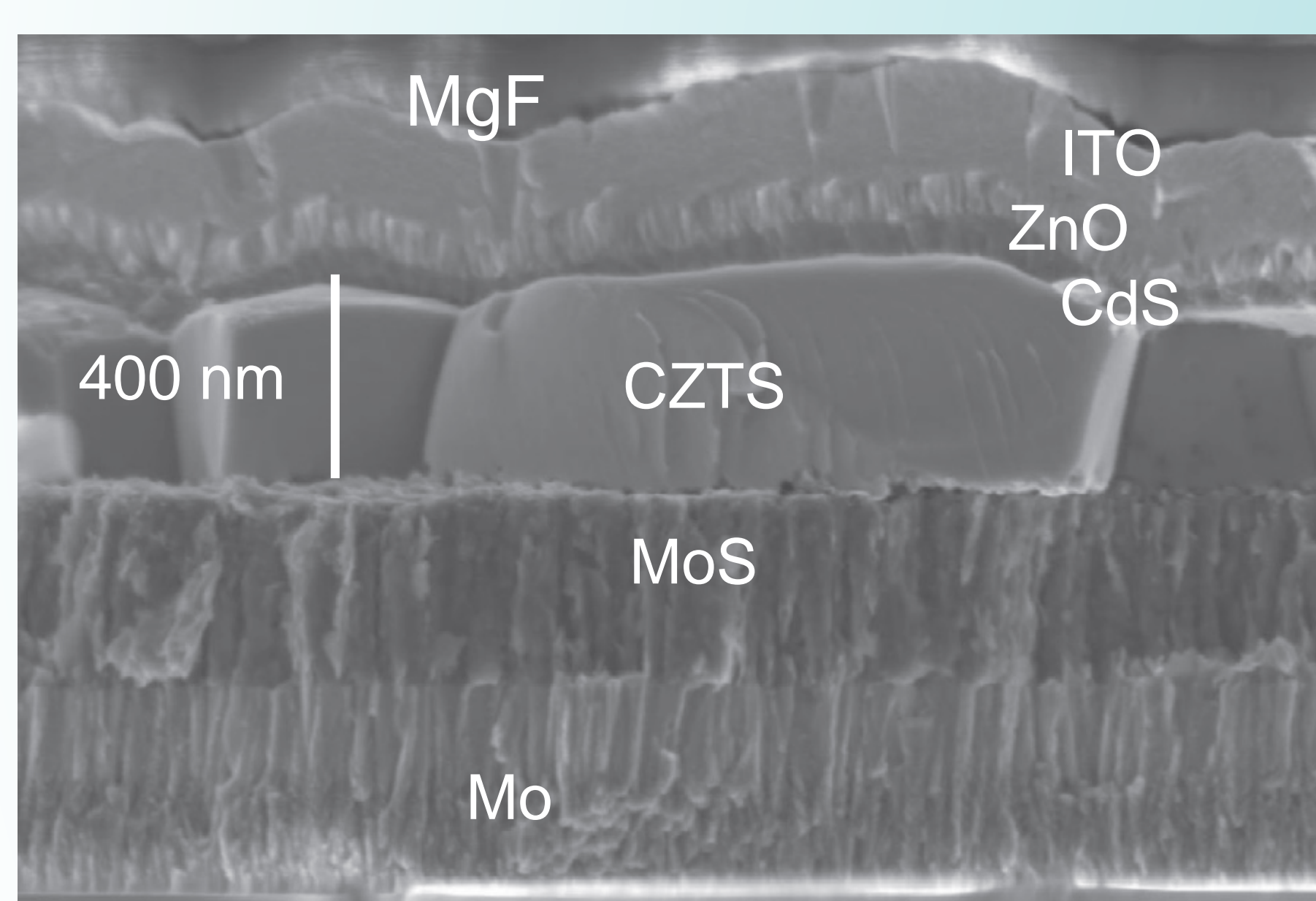
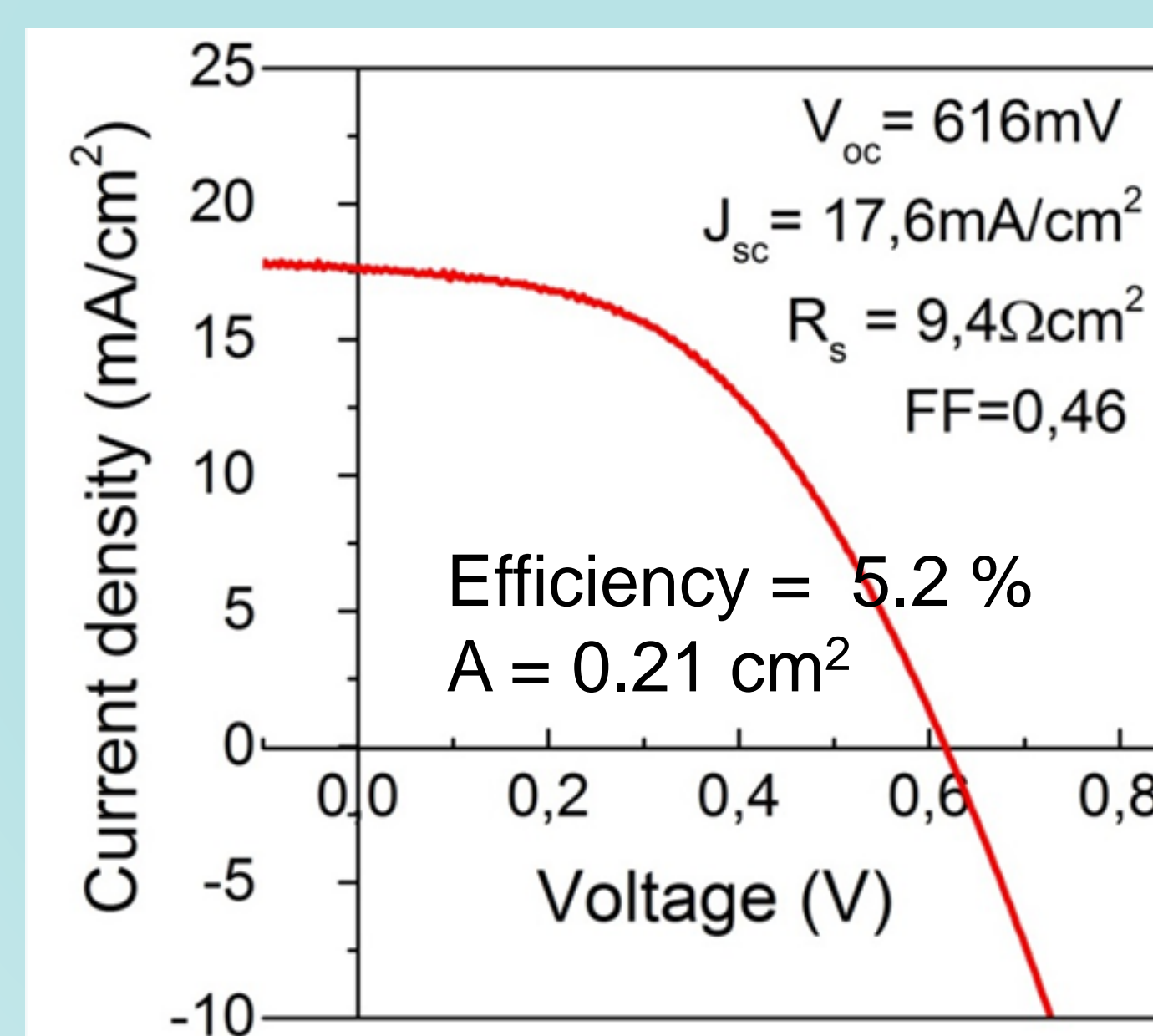


Fig. 6

J-V curve of the champion device at 1 sun



## Conclusion

- A 5.2%-efficiency  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) solar cell has been made by pulsed laser deposition (PLD), the highest value obtained so far with PLD.
- The issues of reproducibility and micro-particulate ejection often encountered with PLD can be solved with a suitable fluence.
- At the optimal laser fluence, amorphous CZTS precursors with optimal stoichiometry for solar cells are deposited from a single target.
- Such precursors do not result in detectable segregation of secondary phases after the subsequent annealing step.
- Material and junction quality with this 400 nm absorber is comparable to that of thicker state-of-the-art CZTS devices.